**Kinetic and equilibrium study of biosorption of Cu & Zn onto Ficus Religiosa**

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**ABSTRACT**

In this study, adsorption of Cu and Zn onto Ficus Religiosa has been investigated. Experimental data have been studied by Five two-parameter models (Langmuir, Freundlich, Stephan Brunauer, Paul Emmett, and Edward Teller (BET), Temkin, Dubinin–Radushkevich), Five three-parameters (Redlich–Peterson, Sips, Toth ,Koble-Corrigan, Radke-Prausnitz) and four kinetic models (Pseudo first order, pseudo second order, the Elovich Kinetic and Weber Morris Kinetic Model. In this study, six non linear error functions (Coefficient of Determination, Sum Squares Errors, Mean Square Error, Root Mean Square Error, Sum of the Absolute Error, Average Relative Error) were examined in order to identify the best adsorption isotherm and kinetic models for Cu and Zn adsorption onto Ficus Religiosa. From the results, it is concluded that three parameters isotherms shows the better fit of the given experimental data as compared to the two parameter isotherms. Among two parameter isotherms, the linear and non-linear forms of Temkin adsorption equilibrium isotherm best fit the given experimental data for Cu & Zn metals. It confirms the formation of unimolecular layer of Cu and Zn by Ficus Religiosa. Apart from three parameter isotherms, the linear and non-linear mathematical forms of Redlich–Peterson adsorption equilibrium isotherm best fit the experimental data for Cu metal adsorption with the closest value of coefficient of correlation to unity. On the other hand, the linear and non-linear forms of Sips adsorption equilibrium isotherm shows the closest fit of the experimental data of Zn adsorption by Ficus Religiosa. Experimental data shows that maximum adsorption capacity of Ficus Religiosa is 28.03 mg/g and 24.89 mg/g for Cu and Zn adsorption respectively. On the other hand, among four adsorption kinetic models, the Elovich kinetic model best fit the given experimental data for Cu and Zn adsorption.

**KEYWORDS** Adsorption, Kinetics, Isotherms, Modeling, Error functions

1. **INTRODUCTION**

In modern era of the world, as the living standard of the people has been highly improved; it results in increasing the number of organic and inorganic pollutant in the atmosphere. Some of which are being degraded by physical, biological and chemical treatments and some cannot be degraded [1, 2]. Cu and Zn are most commonly dangerous heavy metals present in the different industrials wastes and effluents. When these non degradable pollutants mixed with water, it causes the serious human problems as well as to the aquatic life [3]. Among all the available treatments, biological degradation of the organic compounds is extremely low cost and most efficient process. Biosorption is the removal of heavy metals from the waste water by using the inactive, microbial and dead biomass called biomaterials [2,4]. It is an inexpensive and proven technology for the treatment of wastewater and effluents. Actually, in the process of adsorption reveals the capacity of biomaterials to bind the heavy metals from wastewater. These biomaterials are very much cost effective, no additional nutrients are required, and the regeneration of biosorbent is easy [2]. Biosorption is a passive process which does not require energy. There are lots of factors which affect the efficiency of biosorption process. i.e. pH, temperature, concentration and interaction between metallic ions and adsorbents. These factors indicate about the equilibrium of the process which is very much critical for the design of the adsorption equipments [5].

To investigate the comparison and performance of different biosorbent, optimize the design of sorption system, modeling of the isothermal data is very much important [2, 6]. Two, three and even four parameter isothermal models are available for the modeling of adsorption equilibrium data. In most of the modeling processes, two parameter equilibrium isotherms are used due to their simplicity, easy interpretation and well established models [7, 8]. To study the dynamics of the adsorption process with respect to time, the kinetic modeling of the given experimental data is very much important [6, 9].

In the present study, after the collection of experimental data, linear and non-linear regression analysis of Copper and Zinc adsorption onto Ficus Religiosa has been performed. Linear and non-linear mathematical expressions of five two-parameters and five three-parameters [12, 13] are applied to the experimental data of Cu and Zinc adsorption onto Ficus Religiosa and determine the best adsorption isothermal model by using the different error functions. Kinetic study of Cu and Zn adsorption is also carried out in order to study the dynamic of the process [9].

1. **Theoretical Background**

**2.1. Adsorption equilibrium isotherm models**

**2.1.1. Two parameter models**

The mathematical linear, non-linear, identification of different isotherm parameters, abscissa and ordinate of five two-parameter models is given in **Table 1**

**Langmuir adsorption equilibrium isotherm**

In this model, it has been suggested that gaseous molecules adsorbed to the surface of the solids. It is useful for the chemical adsorption as well as physical adsorption [5]. It depends upon the few assumptions i.e. the mechanism of all the adsorbed molecules is same, all adsorption sites are equivalent, molecules on the surface of the adsorbent do not interact with each other, molecules of adsorbate form only monolayer and Structure of adsorbent is homogeneous [14].

**Freundlich adsorption equilibrium isotherm**

It is adsorption isotherm which is a first mathematical fit to the isotherms developed by Freundlich and Küster (1894). It is a purely empirical formula for the gaseous as well as liquid adsorbate. [15]

**Stephan Brunauer, Paul Emmett and Edward Teller (BET) adsorption equilibrium isotherm**

BET adsorption isotherm is most widely applied for multilayer physical adsorption processes. It is basically the extension of Langmuir adsorption isotherm. It is usually applied when there are low pressure systems [13]. To apply the BET adsorption isotherm, following assumptions are made. Enthalpy of the all layers is same; Energy of the all layers is some other than first one, new layer can start before the previous one finished.

**Dubinin–Radushkevich adsorption equilibrium isotherm**

D-R isotherm model is used to analyze the isotherm of high degree of regularity. It is an empirical model which is used for the adsorption of subcritical vapors on to the micro pore solids by a pore filling mechanism [12]. It is usually applied to the heterogeneous surfaces with a mechanism of Gaussain energy distribution. It can also be used for the differentiation of physical and chemical adsorption of metal ions. [16]

**Temkin adsorption equilibrium isotherm**

Temkin adsorption isotherm assumes that decrease in the heat of adsorption is a linear function rather than logarithmic. [8].The adsorption heat of all molecules in the layer would decrease linearly with the coverage due to the adsorbent /adsorbate interactions. It is excellent adsorption isotherm for the determination of gas phase equilibrium. It can be used for the distribution of binding energies. [13].

**2.1.2. Three parameter models**

The mathematical linear, non-linear, identification of different isotherm parameters, abscissa and ordinate of five three-parameter models is given in **Table 1.** List of different parameters appearing in the different models are listed in **Table 2**.

**Redlich–Peterson adsorption equilibrium isotherm**

Redlich and Peterson integrated the features of the Langmuir & Freundlich isotherms into the single equation. In this model, there are three parameters involved in the empirical equation. There is linear dependency on the concentration in the numerator and exponentially increases in denominator to enhance the wide range of concentration of adsorption equilibrium [13]. This model can be applied to the homogeneous as well as heterogeneous surfaces due to its versatility. The Redlich-Peterson adsorption model approaches the Freundlich model at the high concentrations as the exponent “g” approaches to zero. This model resembles the Langmuir adsorption model at low concentration as “g” approaches to unity [17].

**Sips adsorption equilibrium isotherm**

Sips adsorption isotherm is a hybrid form of Langmuir-Freundlich adsorption isotherm model. This empirical equation is actually deduced from the system of heterogeneous adsorption [13].

**Toth adsorption equilibrium isotherm**

It is another empirical model which is helpful for the improvement of Langmuir adsorption isotherm models. This model is also helpful for the heterogeneous adsorption systems which have wide range of applicability from low to high concentration. Toth adsorption isotherm is derived from the potential theory [3, 17].

**Koble-Corrigan adsorption equilibrium isotherm**

It is a well known three-parameter adsorption isotherm model which resembles with the sips adsorption isotherm equilibrium model. Koble –Corrigan also incorporates the features of the Langmuir and Freundlich adsorption equilibrium isotherms for representing the adsorption equilibrium isotherm data [8].

**Radke-Prausnitz adsorption equilibrium isotherm**

This adsorption equilibrium model also incorporates the characteristics of Langmuir and Freundlich adsorption isotherms. When the value of parameters involved approaches to unity, it represents the features of the Langmuir adsorption isotherm. By analyzing the values of the different error functions, it also resembles with Freundlich model [13].

**2.2. Kinetic Models**

List of Differential & integral forms, identification of isotherm parameters and nomination of abscissa and ordinate of four kinetic models is given in **table 3**

**Pseudo 1st order kinetic model**

It is basically 2nd order reactions in which one reactant is present in excess amount and its consumption is negligible in the reaction. As, 2nd order reactions are difficult to handle, i.e. the concentration of two reactants must be followed simultaneously. It has been reduced the order of reaction to pseudo first order reaction for our convenience [10].

Another advantage of using pseudo first order reaction is to determine the rate constant in second-order reaction. These are also useful when one of the reactant is expensive one and other one is cheap. Use the excess amount of relatively cheap component and small amount of expensive one. By, using this, second order rate constant can be evaluated [18].

**Pseudo 2nd order model**

If the sum of the exponent in the rate equation is three and one of the reactant is in excess amount and its consumption within the reaction is negligible then the order of reaction will reduce to the actual one. This type of reaction is termed as pseudo second order reaction [10]. **Elovich model**

It is commonly observed that Elovic equation model is useful for the chemiadsorption processes. It has wide range of application in slow adsorption processes. In some cases, this is also useful for the adsorption of heterogeneous surfaces [14].

**Weber Morris model**

It is an empirical kinetic model which shows that the sorption rate can be controlled by the several factors in the processes like; diffusion of solute from the solution to film surrounding the particles, diffusion from film to the particle surface. It is termed as external diffusion, diffusion from the surface to internal sites. It is termed as surface or pore diffusion, mechanism of uptake, such as physical and chemical sorption, precipitation, ion exchange [7]. It is also observed experimentally that there are four zones of adsorption processes [19].

It is commonly observed that the adsorption of heavy metals from the solution occurred only on the external surface of the adsorbents. All the other parameters for external diffusion model are calculated from the graph. External diffusion model shows the excellent correlation coefficient [11]. It indicates that the adsorption occurs only on the external surfaces of the adsorbents. It is observed in different experiments for the removal of heavy metals that the values of parameter appear in the equation increases with decrease in initial concentration of heavy metal in the solution [20].

**2.3. Error analysis**

It has been commonly observed that linear regression is a vital tool for determining the best agreement between experimental data and mathematical models [8]. In order to find the distribution of adsorbate, six error functions are used in this study. The List of six error functions, mathematical expressions and their abbreviations are enlisted in **Table 4** [13, 19].

1. **RESULTS AND DISCUSSIONS**

 Experimental data of Cu and Zn adsorption onto Ficus Religiosa is co-related with five two-parameters and five three-parameter adsorption isotherm models and four kinetic models. By using the curve fitting tool **(cftool)** available in **MATLAB 7.10.0 (R2010a)**, values of different unknown parameters present in the different linear and non linear forms of adsorption equilibrium models are estimated. By keeping the value of Coefficient of determination “R2” close to unity, values of different parameters are justified. M-files of all adsorption equilibrium and kinetic models are created. Apart from this, in order to check the applicability of any model, the values of six non-linear error functions are calculated and shown in **Table 5 & 6**.

**3.1. Data analysis of adsorption equilibrium isotherms**

**3.1.1. Two parameter isotherms**

If the numbers of unknown parameters in any model equation are two, then it is termed as two parameter adsorption equilibrium isotherms. Applicability of five two-parameter adsorption equilibrium isotherms for given experimental data of Cu and Zn will be explained here. Nomenclature of different terms appearing in the models is shown in **Table 3**. The values of unknown parameters of all two parameter isotherms and six different error functions are give in **Table 5**. Apart from this, Comparison of all five two parameters isotherms for Cu and Zn adsorption is shown in **Figure 1**.

**Langmuir adsorption equilibrium isotherm**

It has been observed that the values of bL and QL are 0.08442(dm3/mg) and 28.03 mg/g for Cu adsorption and 0.03606 (dm3/mg) and 24.89 mg/g for Zn adsorption respectively. Less than unity value of bL indicates the little affinity of adsorbate with the Cu and Zn metal [12]. The non linear error analysis of Langmuir adsorption isotherm also shows the less value of bL and unsatisfactory values of the other error functions. The values of other error functions listed in Table 5 are not acceptable. It results in the unsatisfactory performance of Langmuir adsorption equilibrium isotherm for the given experimental data of Cu and Zn adsorption.

**Freundlich adsorption equilibrium isotherm**

From Table 5, it has been seen that the values of KF and n are 2.943 (l/g) and 2.175 for Cu adsorption, and 1.486 (l/g) and 1.873 for Zn adsorption respectively. The values of n for Cu and Zn adsorption are greater than unity which leads towards the unfavorable condition of adsorption [14]. May be, it will be due to the formation of unimolecular adsorption with homogeneous surface of adsorbent. In spite of having, very high value of “R2” close to unity for both Cu and Zn adsorption, after linear and non-linear analysis of results enlisted in table 5, Freundlich adsorption equilibrium isotherm disqualifies for the given experimental data of Cu and Zn adsorption.

**Stephan Brunauer, Paul Emmett and Edward Teller (BET) adsorption equilibrium isotherm**

Form the **Figure 1**, it is clear that there is no agreement experimental data of Cu and Zn with BET model. The values of qBET and CBET are 21210 mg/g and 0.003197 L/mg for Cu adsorption suggests that the there is no multi layer molecular adsorption [13]. Very high value of qBET and close to zero value of “R2” leads to the rejection of BET adsorption equilibrium isotherm for Cu adsorption. On the other hand, the negative values of the isotherm parameters and close to zero value of “R2” also disqualify the BET model for Zn adsorption equilibrium isotherm.

**Dubinin–Radushkevich adsorption equilibrium isotherm**

From Table 5, it has been observed that the values of isotherm parameters are kD and qD are 0.5 and 20 and 0.897 and 16.73 for Cu & Zn adsorption respectively. The values of qD for Cu and Zn adsorption are within the acceptable range indicating that the adsorption of Cu and Zinc can be the ion exchange process. On the other hand the values of qD for both metals shows the less efficiency of the given adsorption process [12]. This model shows the uptake of the metals is very less by Ficus Religiosa which leads to the poor fit for the given experimental data.

**Temkin adsorption equilibrium isotherm**

From table5,the values of bT and AT are0.6059 (J/mol) & 2.7913 (L/g) for Cu adsorption, 0.6065 (J/mol) & 0.851(L/g) for Zn adsorption respectively. These values of isotherm parameters show that the Temkin adsorption equilibrium isotherm is the best model for the description of the given experimental data. The values of the Temkin constant bT is less than unity for both cases and the value of coefficient of correlation is approaching to unity for both cases also confirms the best applicability of this model for the given experimental data of Cu and Zn. It indicates that the perfect monomolecular layer formation for both metal adsorptions as well as the homogeneity nature of the Ficus Religiosa adsorbent [21, 12].

**3.1.2. Three parameter isotherms**

If the numbers of unknown parameters in any model equation are three, then it is termed as three parameter adsorption equilibrium isotherm. Applicability of five three-parameter adsorption equilibrium isotherms for given experimental data of Cu and Zn is explained here. The values of unknown parameters & six different error functions are given in **Table 6**. Apart from this, Comparison of all five three parameters isotherms for Cu and Zn adsorption is shown in figure 2.

**Redlich–Peterson adsorption equilibrium isotherm**

The values of isotherm parameters and different error functions are enlisted in **Table 6**. The values of KRP, aRP and g are 4.385 (L/g), 0.3848(1/mg) and 0.8328 for Cu adsorption. As it has been observed that the value of g approaches to unity which resemble the adsorption phenomenon to Langmuir adsorption isotherm [10]. It suggests us that the adsorption of Cu by ficus Religiosa is physical adsorption and formation of uni molecular layer is going on [21,24]. The closest to unity, i.e 0.9999 value of coefficient of correlation confirms the best three parameter adsorption models for Cu. On the other hand, 1.7111 (L/g), 0.1028 (1/mg), 0.8333 of KRP, aRP and g are the values isotherm parameters for Zn adsorption by Ficus Religiosa. For that case Zn adsorption, 0.4856 is the value of coefficient of correlation. Very less value of R2 shows the very poor fit of R-P adsorption isotherm for Zn removal by Ficus Religiosa. Unrealistic values of other error functions also help us to omit this model for Zn adsorption.

**Sips adsorption equilibrium isotherm**

From the **Table 6**, the values of isotherm parameters for Cu adsorption are Ks=0.215 L/g, as= 0.0841 L/g and exponent βS =0.942. The values of parameters are very less, which indicates the unfavourability of this model towards the Cu adsorption. Apart from this, the value of coefficient of correlation “R2” is 0.4952 which indicates the disqualification of this model towards the Cu adsorption.

On the other hand the, the values of isotherm parameters for Zn adsorption are Ks=0.12 L/g, aS= 0.13 L/g and exponent βS =0.6. The values of the parameters are within the acceptable range. In spite of this the value of coefficient of correlation “R2” and other error functions indicate the best suitability of sips adsorption equilibrium isotherm for the Zn adsorption by Ficus Religiosa. As we can conclude from the value of βS which lie in between the 0 and 1, the behavior of adsorption of Zn by Ficus Religiosa incorporates the both effect of Langmuir as well as Freundlich [8]. In figure 2, we can see that there is good agreement between the experimental data of Zn adsorption and sips isotherm

**Toth adsorption equilibrium isotherm**

After analysis of results available in table 6, it is concluded that Tooth adsorption model is not suitable for both Copper and Zinc adsorption by Ficus Religiosa.

**Koble-Corrigan adsorption equilibrium isotherm**

The values of isotherm parameters for Cu adsorption are AKC=5, BKC= 0.2781, nKC= 1.324. After analysis of these values, it is concluded that the value of nKC can never be greater than unity for any adsorption process [21]. Inspite of high value of coefficient of correlation R2, probability of KC model for Cu adsorption is omitted.

The values of isotherm parameters for Cu adsorption are AKC=5839, BKC= 1511, nKC= 0.7449. The value of KC constant AKC is very high and the value of coefficient of correlation is also not acceptable [12]. So, KC model also shows the poor fit of given experimental data for Zn adsorption.

**Radke-Prausnitz adsorption equilibrium isotherm**

The values of different isotherm parameters for Cu adsorption are, KR= 2390, kR=0.00016, p = 0.8328. In Table 6, the values of these parameters are acceptable, but the error analysis of this model shows the poor fitting of model towards the Cu adsorption by Ficus Religiosa. On the other hand, the values of different isotherm parameters for Cu adsorption are, KR= 1229, kR=0.0001879, p = 0.6748. The value of kR leads to the disqualification of this model for Zn adsorption by Ficus Religiosa [12].

**3.2. Data analysis of adsorption kinetics**

In order to check the dynamics of adsorption process, kinetic study of the Cu and Zn adsorption has been carried out by using four kinetic models. Values of different parameters and error functions are summarized in **Table 7** for both Cu and Zn adsorption. Graphical comparison of all these four kinetic models can be visualized in **Figure 3.**

 **Pseudo 1st order kinetic model**

The values of kinetic parameters for Cu adsorption are k1=0.0048 (min- 1). And qe1=55 (mg/ g), the value of coefficient of correlation for Cu adsorption is 0.492 which is very much less than that of unity. It leads to the rejection of Pseudo first order kinetic model for Cu adsorption by Ficus Religiosa. On the other hand, For Zn adsorption, the values of parameters are k1=0.000314 (min- 1). And qe1=1082 (mg/ g), again the value of coefficient of correlation is 0.3711 and value of qe1 is much higher which leads towards the very much poor fitting of the first order kinetic model for Zn adsorption[11].

**Pseudo 2nd order kinetic model**

From **Figure 3**, it is clear that there is no relation between the experimental data of Cu and Zn with this model. The values of kinetic parameters K2= 0.4403), qe2 =9.507 for Cu adsorption. The value of coefficient of correlation is 0.638 for Cu adsorption leads to the fitting of Pseudo second order kinetic model for Cu adsorption. For Zn adsorption, the values of the parameters are as follows k2= 0.1724 (g/mg.min), qe2 =8.776 (mg/g) and R2=0.632. These values are also confirms the best fitting of pseudo second order kinetic model [15].

**Elovich kinetic model**

From **Table 7**, it is observed that the values of unknown parameters α= 12900 & β= 1.432 for the case of Cu adsorption. The value of α is realistic and acceptable. On the other hand, value of R2 is 0.9049 which leads to good agreement of the probability of fitting of Elovich model for the given experimental data of Cu adsorption by Ficus Religiosa. Values of kinetic parameters for Zn adsorption are α= 23900 & β= 2.518. The value of α & β are in acceptable range. The value of coefficient of correlation i.e 0.9062 indicates the very much favorable condition of Elovich model for the given experimental data of Zn adsorption by Ficus Religiosa. It confirms the heterogeneous nature of the Ficus Religiosa [7, 22].

**Weber Morris kinetic model**

Form **Figure 3**, it is clear that this model could not be correlated with the experimental data of Cu and Zn adsorption. The values of kinetic parameter **kd =** 0.4187(mg/g.min1/2) , R2 **=**0.5087 and **kd =** 0.4540(mg/g.min1/2 ), R2**=**0.4931 for Cu and Zn adsorption respectively. These values indicate that Weber Morris model does not interpret the given experimental data for Cu and Zn adsorption by Ficus Religiosa [6].

1. **Conclusions**

Following conclusions are drawn from the present study

* Temkin adsorption equilibrium model among five available two-parameter isotherms is shown the best fit of given experimental data for both Cu & Zinc adsorption by Ficus Religiosa. It confirms the mono molecular adsorption of Cu and Zinc onto Ficus Religiosa. It is concluded that surface of adsorbate is homogeneous in nature.
* Redlich-Peterson adsorption equilibrium model, among five three-parameter adsorption isotherms, shows the best agreement of the given experimental data for Cu adsorption by Ficus Religiosa. Sips adsorption equilibrium model, among five three-parameter adsorption isotherms, shows the best fitness of the given experimental data for Zn adsorption by Ficus Religiosa.
* For kinetic study, among four kinetic models, the Elovich kinetic model best fit according to the given experimental data of Cu & Zn adsorption. It confirms the physical adsorption of the Cu and Zn onto Ficus Religiosa.
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1. **References**

 [1] Visekruna, A. Anita, S. Marinic P.L; H A to Environment 1(1), 29-37 (2011)

[2] Wang, X.S. Zhong, L. Sun, C.; Desalination, 235, 146–159 (2009).

[3] Shan, Y.H. Wang, C.C.; Journal of Hazardous Materials 156, 398–404 (2008)

[4] Srihari, V. Ashutosh, D.; Ecotoxicology and Environmental Safety 71, 274–283 (2008).

[5] Foo, K.Y. and Hameed, B.H.; J. Chemical Engineering. , 2(10), 156 (2010).

[6] Yahya, S. Al-Degs, Musa I. El-Barghouthi, Ayman, A. Issa, Majeda, A. Khraisheh, G. and Walker, M.; Water Research, 40 , 2645 – 2658 (2006)

[7] Kazmi\*, M. Saleemi, A.R. Feroze, N. Yaqoob, A. Ahmad, S.W.; P Journal of Chemical Technology,15 (2),1-6 ,0016(2013)

[8] ozdemir. C.S. and Önal, Y.; Particulate Science and Technology, 10.1080, 02726351(2013)

[9] Unamuno , V.I.R Visscher, A. D. Lesage, E. Meers, E. Leuridan, I.; Chemosphere, 69, 1136–1143 (2007)

[10] Junxiong, L. , WANG, L Front. Environ. Sci. Engin. China. , 3(3), 320–324 (2009)

[11] Feroze, N. Kazmi†, M and Ramzan, N.; Korean J. Chem. Eng., 30(1), 95-100 (2013)

 [12] Vijayaraghavan, K. Padmesh, T.V.N. Palanivelu, K. and Velan, M.; J. Hazardous Materials,B133, 304–308 (2006)

[13] John, U. Oubagaranadin, K. Murthy, Z.V.P. and Rao, P.S.; Indian Institute of Chemical Engineers ,3(49), 196-204 (2007)

[14] Kazmi, M. Feroze, N. Javed, H. Zafar, M. and Ramzan\*, N.; J.Chem.Soc.Pak,34 (6),1357 (2012)

[15] Kazmi†, M. Feroze, N. Naveed, S. and Javed, S.H ., Korean J. Chem. Eng., 28(10), 2033-2040 (2011)

[16] Kailas L. Wasewar, Kumar, S. and Prasad, B. .; J. Environmental Protection Science 3, 41 – 52 (2009)

[17] Chan, L.S. Cheung, W.H. Allen, S.J. and McKay, G.; Chinese Journal of Chemical Engineering, 20(3), 535—542 (2012)

[18] Nwabbanne, J.T and lgbokwe, P.K., Journals of Engineering and Applied Sciences 3(11), 829-864(2008)

[19] Wu, F.C. Tseng, R.L. Juang, R.S.; Chemical Engineering Journal. ,153 ,1–8 (2009)

 [20] Igwe, J. C. and Abia, A. A.; International Journal of Physical Sciences 2 (5),119-127, (2007)

 [21] Yu, L. Jua, Y.L., Separation and Purification Technology 61, 229–242(2008)

[22] Hui QIU, Lu LV, Bing-cai PAN†, Zhang, Q.J. Zhang, W. M. Zhang, Q. X.; Journal of Zhejiang University,10(5) 716-7242009

[23] Chilev, C. I. Pentchev, F. Darcrim-Lamari, E. Simeonov,; Journal of the University of Chemical Technology and Metallurgy, 5(47) , 540-545 (2012)

 [24] Gimbert, F. Nadia, M.C., Renault, F. Badot, P.M. Crini , G.; Journal of Hazardous Materials 157, 34–46 (2008)

**Table 1** List of Linear, Non Linear forms, identification of isotherm parameters and nomination of abscissa and ordinate of five two-parameters and five three-parameter adsorption equilibrium isotherm models

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sr.#** | **Isotherm** | **Non Linear Form** | **Linear Form** | **Parameters** | **Plot(Y,X)** |
| 1 | Langmuir |  |  | bL & QL | Ce/qe vs Ce |
| 2 | Freundlich |  |  |  |  |
| 3 | BET |  |  |  |  |
| 4 | Dubinin–Radushkevich |  |  | *qD, kD* |  |
| 5 | Temkin |  |  |  |  |
| 6 | Redlich–Peterson(RP) |  |  | *aRP, g, KRP* |  |
| 7 | Sips |  |  |  |  |
| 8 | Toth |  |  |  |  |
| 9 | Koble-Corrigan(KC) |  |  | AKC,BKC,nKC |  |
| 10 | Radke-Prausnitz(R) |  |  |  |  |

**Table 2** Nomenclature

|  |
| --- |
| AT Temkin adsorption equilibrium binding constant (L/g)AKC Koble-Corrigan isotherm constant(Ln mg1-n/g)  aRP the Redlich–Peterson model constant (1/mg) α initial sorption rate (mg./g.min) αT Toth adsorption isotherm constant (L/mg)aS Sips model constant (L/mg), BKC  Koble-Corrigan isotherm constant(L/mg)n L Langmuir isotherm model constant (dm3/mg)bT Temkin constant related to the adsorption heat (J/mol) β desorption rate constant (mg/.g .min) βS Sips adsorption model exponentCS adsorbate monolayer saturation concentration (mg/L) CBET  BET adsorption isotherm relating to energy of the surface interaction (L/mg).Ce equilibrium concentration of adsorbate (mg/L)ε Dubinin–Radushkevich constant  g the Redlich–Peterson model exponent kD Dubinin–Radushkevich model isotherm constant (mol2/KJ2)KF Freundlich isotherm Constant (l/g)kT Toth adsorption isotherm constant (mg/g)KR Radke-Prausnitz isotherm model constant KRP is Redlich–Peterson isotherm constant (L/g) kR Radke-Prausnitz isotherm model constantKS Sips model isotherm constant (L/g) kd the internal diffusion coefficient (mmol/g.min1/2) k1  rate constant at equilibrium for pseudo first order sorption (min- 1) k2 pseudo-second-order rate constant for the adsorption process (g/mg.min) n Freundlich exponentnKC adsorption intensityp Model exponent qe amount of the adsorbate in adsorbent at equilibrium (mg/g) qBET theoretical isothermal saturation capacity (mg/g) qD theoretical isothermal saturation capacity (mg/g)qt  amount of the solute sorbed at time t ( mg/ g) QL maximum mono-layer coverage capacities (mg/g)R General Gas Constant,T Absolute temperature in Kelvin t Tooth model exponent  |

**Table 3** List of Differential & integral forms, identification of isotherm parameters and nomination of abscissa and ordinate of four kinetic models

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sr.#** | **Kinetic Model** | **Differential Form** | **Integral Form** | **Plot(Y,X)** |
| 1 | Pseudo-first-order(PFO) |  |  | ln (qe1 – qt) vs t  |
| 2 | Pseudo-Second order(PSO) |  |  |  |
| 3 | The Elovic Kinetic Model |  |  | qt vs ln(t)  |
| 4 | Weber Morris model |  |  qt vs t  |

**Table 4** Mathematical expressions and abbreviations of six non linear error functions

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr.#** | **Name** | **Abbreviation** | **Mathematical Expression** |
| 1 | Coefficient of Determination | R2 |  |
| 2 | Sum Squares Errors | SSE |  |
| 3 | Mean Square Error | MSE |  |
| 4 | Root Mean Square Error | RMSE |  |
| 5 | Sum of the Absolute Error | SAE / EABS |  |
| 6 | Average Relative Error | ARE |  |

**Table 5** Values of unknown Coefficients of five two-parameter isotherms for the bio sorption of Cu & Zn onto the Ficus Religiosa & Error Functions. i.e. R2, SSE, MSE, RMSE, SAE & ARE

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. #** | **Equilibrium isotherm** | **Values of unknown coefficients** | **Values of different error functions** |
| **1** | **Langmuir** |  **(dm3/mg)** | **QL**(mg/g) | **R2** | **SSE** | **MSE** | **RMSE** | **SAE** | **ARE** |
| **Cu** | **Linear** | 0.084 | 28.03 | 0.974 | 0.373 | 0.047 | 0.216 | 1.537 | 27.161 |
| **Non-Linear** | 0.079 | 27.02 | 0.505 | 22748 | 2843 | 53.325 | 249.63 | 153.762 |
| **Zn** | **Linear** | 0.036 | 24.89 | 0.972 | 0.874 | 0.109 | 0.331 | 1.923 | 14.986 |
| **Non-Linear** | 0.012 | 24.96 | 0.647 | 2023 | 252.97 | 15.905 | 75.96 | 73.016 |
| **2** | **Freundlich** |  **(l/g)** | **n** | **R2** | **SSE** | **MSE** | **RMSE** | **SAE** | **ARE** |
| **Cu** | **Linear** | 2.943 | 2.175 | 0.976 | 0.129 | 0.016 | 0.127 | 0.825 | -220.614 |
| **Non-Linear** | 9.712 | 63.24 | 0.001 | 839.15 | 104.894 | 10.242 | 71.253 | 186.732 |
| **Zn** | **Linear** | 1.486 | 1.873 | 0.975 | 0.118 | 0.0147 | 0.121 | 0.822 | -51.118 |
| **Non-Linear** | 0.302 | 2.79 | 0.003 | 1379 | 172.39 | 13.132 | 85.342 | 86.508 |
| **3** | **BET** |  **(mg/g)** | **CBET**(L/mg) | **R2** | **SSE** | **MSE** | **RMSE** | **SAE** | **ARE** |
| **Cu** | **Linear** | 21210 | 0.001 | 0.162 | 0.0291 | 0.004 | 0.060 | 0.373 | 487.082 |
| **Non-Linear** | 2.082 | 15480 | 0.979 | 2181 | 272.65 | 16.512 | 98.28 | 304.515 |
| **Zn** | **Linear** | -0.0024 | -1.79 | 0.453 | 349590 | 436980 | 661.047 | 37923 | 132140 |
| **Non-Linear** | -0.495 | -5.84 | .0007 | 12122 | 151.53 | 12.312 | 67.192 | 99.942 |
| **4** | **Dubinin–Radushkevich** |  **(mol2/KJ2)** | **qD (mg/g)** | **R2** | **SSE** | **MSE** | **RMSE** | **SAE** | **ARE** |
| **Cu** | **Linear** | 0.5 | 20 | 0.998 | 0.8 | 0.1 | 0.316 | 2.243 | -238.169 |
| **Non-Linear** | 2.125 | 24.78 | 0.874 | 147.33 | 18.416 | 4.291 | 27.643 | 1290 |
| **Zn** | **Linear** | 0.897 | 16.73 | 0.997 | 0.832 | 0.104 | 0.323 | 2.235 | 9.182 |
| **Non-Linear** | 5.483 | 22.21 | 0.774 | 204.32 | 25.517 | 50.514 | 30.382 | 1068 |
| **5** | **Temkin** |  **(J/mol)** | AT **(L/g)** | **R2** | **SSE** | **MSE** | **RMSE** | **SAE** | **ARE** |
| **Cu** | **Linear** | 0.606 | 2.791 | 0.984 | 12.49 | 1.561 | 1.254 | 9.051 | 30.871 |
| **Non-Linear** | 0.606 | 2.79 | 0.984 | 12.487 | 1.561 | 1.256 | 9.051 | 30.872 |
| **Zn** | **Linear** | 0.606 | 0.85 | 0.971 | 16.159 | 2.02 | 1.421 | 10.738 | 34.697 |
| **Non-Linear** | 0.606 | 0.85 | 0.971 | 16.1591 | 2.02 | 1.421 | 10.738 | 34.697 |

**Table 6** Values of unknown Coefficients of five three-parameter Isotherm models for the bio sorption of Cu and Zn onto the Ficus Religiosa & Error Functions. i.e R2, SSE, MSE & RMSE

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr.#** | **Equilibrium Model** | **Values of Unknown Coefficients** | **Values of Different Error Functions** |
| **1** | **Redlich–Peterson (RP)** | **kRP(L/g)** | **aRP(1/mg)** | **g** | **R2** | **SSE** | **MSE** | **RMSE** | **SAE** | **ARE** |
| **Cu** | **Linear** | 4.385 | 0.3848 | 0.8328 | 0.9992 | 0.015 | 0.0065 | 0.0804 | 0.4966 | 7.8556 |
| **Non-Linear** | 5.649 | 0.5824 | 0.8026 | 0.9963 | 2.88 | 0.3610 | 0.6008 | 3.5288 | 7.8271 |
| **Zn** | **Linear** | 1.711 | 0.1028 | 0.8333 | 0.4860 | 42.0185 | 5.2523 | 2.2918 | 13.3768 | 34.3425 |
| **Non-Linear** | 1.297 | 0.1324 | 0.8334 | 0.9951 | 4.7448 | 0.5931 | 0.7701 | 4.8340 | 12.4279 |
| **2** | **Sips** | **KS(L/g)** | **aSL/mg)** | **βS** | **R2** | **SSE** | **MSE** | **RMSE** | **SAE** | **ARE** |
| **Cu** | **Linear** | 0.215 | 0.0841 | 0.492 | 0.4324 | 3.159 | 0.3949 | 0.6284 | 4.4288 | 57.0048 |
| **Non-Linear** | 4.107 | 0.1118 | 0.6004 | 0.4951 | 3.817 | 0.477 | 0.6908 | 4.4762 | 16.9545 |
| **Zn** | **Linear** | 0.12 | 0.13 | 0.6 | 0.9122 | 2.9696 | 0.371 | 0.6093 | 4.19 | 82.35 |
| **Non-Linear** | 0.91 | 0.0088 | 0.71 | 0.8796 | 149 | 18.86 | 4.329 | 149 | 24.60 |
| **3** | **Tooth** | **KT(mg/g)** | **aT (L/mg)** | **t** | **R2** | **SSE** | **MSE** | **RMSE** | **SAE** | **ARE** |
| **Cu** | **Linear** | 52.4 | 10.55 | 7.876 | 0.9785 | 0.2486 | 0.0308 | 0.1756 | 1.1767 | 11.9799 |
| **Non-Linear** | 541.2 | 12.54 | 20.06 | 0.9758 | 21.4496 | 2.6812 | 1.6374 | 10.9058 | 21.3660 |
| **Zn** | **Linear** | 1.653 | 90 | 69000 | 0.5517 | 26.344 | 3.2930 | 1.8143 | 12.2249 | 82.5748 |
| **Non-Linear** | 1.653 | 0.8008 | 0.1152 | 0.1043 | 350.254 | 43.7818 | 6.6168 | 48.7713 | 183.9364 |
| **4** | **Koble-Corrigan(KC)** | **AKC(Ln)**  | **BKC(L/mg)n** | **nKC** | **R2** | **SSE** | **MSE** | **RMSE** | **SAE** | **ARE** |
| **Cu** | **Linear** | 5.084 | 0.2781 | 1.324 | 0.9952 | 0.0039 | 0.00049 | 0.0222 | 0.1532 | 21.7299 |
| **Non-Linear** | 4.107 | 0.1118 | 0.6004 | 0.9951 | 3.8175 | 0.4772 | 0.6908 | 4.4762 | 16.9545 |
| **Zn** | **Linear** | 5839 | 1511 | 0.7449 | 2.7\*10-08 | 0.9807 | 0.1226 | 0.3501 | 1.8884 | 193.45 |
| **Non-Linear** | 1.513 | 0.05001 | 0.7449 | 0.9919 | 4.499 | 0.5624 | 0.7499 | 4.499 | 15.289 |
| **5** | **Radke-Prausnitz(R)** | **KR** | **kR** | **pR** | **R2** | **SSE** | **MSE** | **RMSE** | **SAE** | **ARE** |
| **Cu** | **Linear** | 2390 | 0.00016 | 0.8328 | 1.8\*10-08 | 63.64 | 7.956 | 2.82 | 19.098 | 373.77 |
| **Non-Linear** | 1.584 | 10920 | 0.4486 | 0.895 | 120.03 | 15.004 | 3.8735 | 25.58 | 32.47 |
| **Zn** | **Linear** | 1229 | 0.0001879 | 0.6748 | 0.9064 | 115.0276 | 14.3784 | 3.7919 | 25.4365 | 171.032 |
| **Non-Linear** | 1.95 | 0.5587 | 0.5334 | 5.2\*10-9 | 60.3199 | 7.5400 | 2.7459 | 18.006 | 27.6950 |

**Table 7** Values of coefficients of different kinetic models & Error functions R2, SSE, and MSE & RMSE for Cu and Zn adsorption

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr.#** | **Kinetic Model** | **Values of Unknown Coefficients** | **Values of Error Functions** |
| **1** | **Pseudo First Order of Lagergren (PFO)** | **k1(1/min)** | **qe1(mg/g)** | **R2** | **SSE** | **MSE** | **RMSE** |
| **Cu** | 0.0048 | 55 | 0.492 | 0.0999 | 0.012 | 0.112 |
| **Zn** | 0.0003146 | 1082 | 0.3711 | 0.0007044 | .00008805 | .0094 |
| **2** | **Pseudo 2nd Order (PSO)** | **k2(g/mg.min)** | **qe2 (mg/g)** | **R2** | **SSE** | **MSE** | **RMSE** |
| **Cu** | 0.4403 | 9.507 | 0.638 | 0.0086 | 0.0011 | 0.0328 |
| **Zn** | 0.1724 | 8.776 | 0.632 | 0.0261 | 0.0033 | 0.0571 |
| **3** | **The Elovich kinetic model** | **α(mg/g.min)** | **β(mg/g.min)** | **R2** | **SSE** | **MSE** | **RMSE** |
| **Cu** | 12900 | 1.432 | 0.9049 | 143.6175 | 17.9522 | 4.2370 |
| **Zn** | 23900 | 2.518 | 0.9062 | 0.2273 | 0.0284 | 0.1686 |
| **4** | **Weber Morris kinetic model** | **kd(mg/g.min1/2 )** | **R2** | **SSE** | **MSE** | **RMSE** |
| **Cu** | 0.4187 | 0.5087 | 177.753 | 22.220 | 4.714 |
| **Zn** | 0.4540 | 0.4931 | 222.487 | 27.8061 | 5.2731 |

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**Figure 1** Comparison of five two-parameter adsorptionisotherm models

1. For **Cu** adsorption
2. For **Zn** adsorption



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**Figure 2** Comparison of five, three-parameter adsorptionisotherm models

1. For Cu adsorption (b) For Zn adsorption





**Figure 3** Comparison of different kinetic models of **Cu & Zn** adsorptio**n** onto Ficus Religiosa